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XVI.

OPTICAL NOTICES.

By Wolcott Gibbs, M.D.

Presented, April 13, 1875.

I.—ON A NEW OPTICAL CONSTANT.

When a plate of glass with plane and parallel surfaces is placed in the field of the spectroscope in such a manner that one half of the bundle of rays incident upon the first surface of the prism passes through the glass, a series of interference bands will be seen in the spectrum, known from their discoverer as Talbot's bands. When the mean index of refraction of the glass plate is less than the mean index of the prism, the plate must be so placed as to receive the rays which fall upon the prism nearest its refracting edge; in the opposite case, so as to receive the rays which fall upon the prism nearest its base. A plate of any transparent medium not doubly refracting may be made to exhibit similar bands in the spectrum. Doubly refracting plates produce two sets of bands, corresponding respectively to the ordinary and extraordinary rays. In any isotropic substance, the number of bands, τ, between any two lines in the spectrum the indices of which are n_2 and n_1, may be found from the expression,

$$\tau = \theta \left\{ (n_2 - 1) \frac{1}{\lambda_2} - (n_1 - 1) \frac{1}{\lambda_1} \right\}$$

in which θ represents the thickness of the plate, and λ_2 and λ_1 the wave lengths in air of the two rays corresponding to n_2 and n_1.

The formula which I have given is familiar to all who have paid attention to the beautiful and fertile theory of interferences. It forms the starting-point of my investigation.

If we take θ as unity, the formula

$$\tau = (n_2 - 1) \frac{1}{\lambda_2} - (n_1 - 1) \frac{1}{\lambda_1}$$

will give the number of dark bands for a plate having the unit of thickness, which, if λ_2 and λ_1 be expressed in fractions of a millimeter, will be one millimeter. If now we divide the expression given by the density of the substance of which the plate is composed, d, we shall have

$$I = \frac{\tau}{d} = \frac{1}{d} \left\{ (n_2 - 1) \frac{1}{\lambda_2} - (n_1 - 1) \frac{1}{\lambda_1} \right\}$$

The quantity I, as thus defined, I call the "interferential constant." It expresses the number of bands in the spectrum between two rays the indices of which for the given plate are n_2 and n_1, for a thickness of the plate equal to a unit of density. I shall endeavor to show, by the discussion of a number of observations, that the quantity I is for each substance a characteristic optical function which, for all the cases which the present state of science enables us to discuss, is independent of the temperature, and which may therefore be regarded as a new physical constant.

For the purpose of testing the character and value of the new constant, I have selected the extensive series of observations made by Wüllner* in his examination of the function $\frac{n-1}{d}$, a function which Landolt and Dale and Gladstone in their extended investigations have assumed to be constant for the same ray and the same substance. Wüllner determined with great care the indices of refraction of a series of liquids for the three hydrogen lines C, F, and G at different temperatures, together with the corresponding densities. He found that, for very considerable ranges of temperature, the three indices and the corresponding densities could be represented very closely by linear functions of the form $n = n_o - kt$ and $d = d_o - bt$. Wüllner's general results are given in Table I., in which $N\alpha$ and $N\gamma$ represent the indices of refraction at $O° C$ for the rays C and G, d and T the corresponding densities and temperatures.

With the data here reproduced, Wüllner computed for each liquid the value of the function $\frac{A-1}{D}$, in which A represents the term in Cauchy's formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

which is independent of the wave length, and D the density. The general result of his investigation is that the functions $\frac{A-1}{D}$ or $\frac{n-1}{d}$ cannot be regarded as perfectly constant, either when the densities are made to vary by heating or cooling or by mixing one liquid with another.

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* Pogg. Ann., T. 133, p. 1.

TABLE I.

SUBSTANCE.	$Na - kT$.	$N\gamma - k'T$.	$d - bT$.
Water	1.333138 — 0.000099 T	1.342290 — 0.000099 T	— — — —
Alcohol	1.368431 — 0.000389 T	1.378158 — 0.000395 T	0.81328 — 0.000850 T
Glycerine *a*	1.453177 — 0.000265 T	1.465064 — 0.000267 T	1.23454 — 0.000630 T
„ 3.7 Water 1 . .	1.426172 — 0.000231 T	1.437604 — 0.000233 T	1.18598 — 0.000557 T
„ 1. „ 1 . .	1.389760 — 0.000185 T	1.400239 — 0.000187 T	1.11500 — 0.000444 T
„ 0.5 „ 1 . .	1.369609 — 0.000154 T	1.379567 — 0.000156 T	1.07549 — 0.000365 T
Glycerine *b*	1.463651 — 0.000270 T	1.475732 — 0.000272 T	1.25073 — 0.000635 T
„ 4. Alcohol 1 . .	1.442453 — 0.000292 T	1.454235 — 0.000296 T	1.14155 — 0.000660 T
„ 2. „ 1 . .	1.428029 — 0.000305 T	1.439160 — 0.000310 T	1.07420 — 0.000725 T
„ 0.998 „ 1 . .	1.411538 — 0.000330 T	1.422213 — 0.000336 T	0.99748 — 0.000750 T
„ 0.4997 „ 1 . .	1.398365 — 0.000356 T	1.408848 — 0.000363 T	0.93710 — 0.000805 T
Conc. Solution of $ZnCl_2$ . . .	1.509257 — 0.000288 T	1.528169 — 0.000291 T	1.96816 — 0.001153 T
„ 3.997 Water 1 . .	1.460379 — 0.000266 T	1.476405 — 0.000268 T	1.68519 — 0.000992 T
„ 1.9996 „ 1 . .	1.433093 — 0.000258 T	1.447567 — 0.000261 T	1.52457 — 0.000882 T
„ 0.9998 „ 1 . .	1.404593 — 0.000250 T	1.417494 — 0.000252 T	1.36623 — 0.000793 T
Carbonic Disulphide	1.634066 — 0.000780 T	1.692149 — 0.000850 T	1.29366 — 0.001506 T
„ 3.955 Alcohol 1 . .	1.551274 — 0.000678 T	1.594015 — 0.000750 T	1.14913 — 0.001373 T
„ 2.12836 „ 1 . .	1.512477 — 0.000626 T	1.547691 — 0.000680 T	1.08033 — 0.001294 T
„ 1.03111 „ 1 . .	1.465695 — 0.000560 T	1.492206 — 0.000590 T	0.99533 — 0.001178 T

Taking the data of Table I., I have computed the values of the interferential constant *I* for at least three different temperatures in the case of each liquid. Five determinations are given in the case of water, and four in the case of carbonic disulphide. As the density of water, even for a limited range of temperature, cannot be expressed by a linear function, I have computed it from the volumes as given by Pierre. My general results are given in Table II.

TABLE II.

Na.	*Nγ.*	*T.*	*d.*	*I.*	*τ.*
		WATER.			
1.333138	1.342290	0°	1.00000	287.1	287.0
1.332148	1.341300	10°	0.99988	286.3	286.3
1.331158	1.340310	20°	0.99839	285.9	285.5
1.330168	1.339320	30°	0.99588	285.8	284.7
1.329178	1.338330	40°	0.99250	285.8	282.9
			Mean,	286.2	
					$\tau = 287.0 - 0.0775\,T$.
		CARBONIC DISULPHIDE.			
1.634066	1.692149	0°	1.29366	495.2	640.7
1.622366	1.679399	15°	1.27107	494.8	628.9
1.610666	1.666649	30°	1.24848	494.3	617.1
1.596626	1.651349	48°	1.22137	493.6	603.0
			Mean,	494.77	
					$\tau = 640.7 - 0.7853\,T$.
		ALCOHOL.			
1.368431	1.378158	0°	0.81281	389.4	316.5
1.362596	1.372233	15°	0.80003	389.5	311.6
1.356761	1.366308	30°	0.78731	389.6	306.7
			Mean,	389.5	
					$\tau = 316.5 - 0.3266\,T$.
		CHLORIDE OF ZINC.			
Saturated solution of $ZnCl_2$.					
1.509257	1.528169	0°	1.96816	228.7	450.2
1.503497	1.522349	20°	1.94510	228.9	445.4
1.497737	1.516529	40°	1.92204	229.2	440.7
			Mean,	228.9	
					$\tau = 450.2 - 0.2375\,T$.
Water, 1.	Sat. solution of $ZnCl_2$, 3.997.				
1.460379	1.476405	0°	1.68519	239.9	404.3
1.455059	1.471045	20°	1.66535	240.3	400.2
1.449739	1.465685	40°	1.64551	240.5	395.8
			Mean,	240.2	
					$\tau = 404.3 - 0.2125\,T$.

TABLE II. (*continued*).

CHLORIDE OF ZINC.

Water, 1. Sat. solution of $ZnCl_2$, 1.9996.

N_a.	N_γ.	T.	d.	I.	τ.
1.433093	1.447567	0°	1.52457	248.6	379.1
1.427933	1.442347	20°	1.50693	248.7	374.8
1.422773	1.437127	40°	1.48929	248.8	370.6

Mean, 248.7

$\tau = 379.1 - 0.2125\ T.$

Water, 1. Sat. solution of $ZnCl_2$, 0.9998.

1.404593	1.417494	0°	1.36623	258.2	352.7
1.399593	1.412454	20°	1.35037	258.2	348.7
1.394593	1.407414	40°	1.33451	258.2	344.6

Mean, 258.2

$\tau = 352.7 - 0.2025\ T.$

GLYCERINE *a* AND WATER.

Glycerine *a*.

1.453177	1.465064	0°	1.23454	315.2	389.1
1.449202	1.461059	15°	1.22509	314.9	385.9
1.446552	1.458389	25°	1.21879	314.8	383.7
1.442577	1.454384	40°	1.20934	314.6	380.5

Mean, 314.9

$\tau = 389.1 - 0.2150\ T.$

Water, 1. Glycerine, 3.7.

1.426172	1.437604	0°	1.18598	309.1	366.6
1.422456	1.434109	15°	1.17763	309.2	364.1
1.420397	1.431779	25°	1.17206	308.8	361.8
1.416932	1.428284	40°	1.16370	308.5	359.0

Mean, 309.0

$\tau = 366.6 - 0.1900\ T.$

Water, 1. Glycerine, 1.

1.389760	1.400239	0°	1.11500	300.7	335.3
1.386985	1.397434	15°	1.10834	300.4	333.0
1.385135	1.395564	25°	1.10390	300.2	331.4
1.382360	1.392759	40°	1.09724	299.9	329.1

Mean, 300.4

$\tau = 335.3 - 0.1550\ T.$

Water, 1. Glycerine, ½.

1.369609	1.379567	0°	1.07549	295.6	317.9
1.367299	1.377227	15°	1.07002	295 3	316.0
1.365759	1.375667	25°	1.06637	295.2	314.8
1.363449	1.373327	40°	1.06089	294.9	312.9

Mean, 295.2

$\tau = 317.9 - 0.1250\ T.$

TABLE II. (*continued*).

GLYCERINE *b* AND ALCOHOL.

Glycerine *b*.

$N\alpha$.	$N\gamma$.	T.	d.	I.	τ.
1.463651	1.475732	0°	1.25073	318.2	398.0
1.459601	1.471652	15°	1.24120	317.9	394.6
1.455551	1.467572	30°	1.23160	317.7	391.3
			Mean,	317.9	

$\tau = 398.0 - 0.2233\ T.$

Alcohol, 1. Glycerine *b*, 4.

1.442453	1.454235	0°	1.14155	333.0	380.2
1.438073	1.449795	15°	1.13165	332.8	376.6
1.433693	1.445355	30°	1.12175	332.5	373.0
			Mean,	332.7	

$\tau = 380.2 - 0.2400\ T.$

Alcohol, 1. Glycerine, 2.

1.428029	1.439160	0°	1.07420	342.0	367.4
1.423454	1.434510	15°	1.06333	341.9	363.5
1.418879	1.429860	30°	1.05245	341.7	359.6
			Mean,	341.9	

$\tau = 367.4 - 0.2600\ T.$

Alcohol, 1. Glycerine, 0 998.

1.411538	1.422213	0°	0.99750	353.9	353.1
1.406588	1.417173	15°	0.98623	353.8	348.9
1.401638	1.412133	30°	0.97498	353.5	344.6
			Mean,	353.7	

$\tau = 353.1 - 0.2833\ T.$

Alcohol, 1. Glycerine, 0.4997.

1.398365	1.408848	0°	0.93710	364.4	341.5
1.393025	1.403403	15°	0.92503	364.9	337.5
1.387685	1.397958	30°	0.91295	364.8	333.0
			Mean,	364.7	

$\tau = 341.5 - 0.2853\ T.$

ALCOHOL AND CS_2.

Alcohol, 1. CS_2, 3.955.

1.551274	1.594015	0°	1.149130	468.9	538.9
1.541104	1.582765	15°	1.128540	468.1	528.3
1.530934	1.571515	30°	1.107940	467.7	517.7
			Mean,	468.2	

$\tau = 538.9 - 0.7066\ T.$

Alcohol, 1. CS_2, 2.12836.

1.512477	1.547691	0°	1.080130	454.2	490.6
1.503087	1.537491	15°	1.060720	453.7	481.2
1.493697	1.527291	30°	1.041310	453.1	471.9
			Mean,	453.7	

$\tau = 490.6 - 0.6233\ T.$

TABLE II. (*continued*).

ALCOHOL AND CS_2.

Alcohol, 1.	CS_2, 1.03111.				
$N\alpha$.	$N\gamma$.	T.	d.	I.	τ.
1.465695	1.492206	0°	0.995330	435.0	433.0
1.457295	1.483356	15°	0.977660	435.0	425.3
1.448895	1.474506	30°	0.959990	434.9	417.5
			Mean,	435.0	

$\tau = 433 - 0.5166\, T$.

In this table, $N\alpha$ and $N\gamma$ represent the indices of refraction of the substances named at the temperature T, d the corresponding densities, and I the interferential constants. The indices and densities are computed from Wüllner's formulas given in Table I. Each of these linear formulas was deduced from a large number of direct observations made at different accurately observed temperatures. The values of the indices and densities calculated from them are therefore more reliable than those obtained by single direct observations. In the cases of all the substances examined, Table II. shows clearly that the interferential constants are, for very considerable ranges of temperature, independent of the temperature itself. Wüllner's formulas cited in Table I. show that in all cases the co-efficients k and k' are very nearly equal, so that $N\alpha$ and $N\gamma$ decrease very nearly in the same ratio as the temperature rises. The formula defining the interferential constant,

$$I = \frac{1}{d}\left\{(n_2-1)\frac{1}{\lambda_2} - (n_1-1)\frac{1}{\lambda_1}\right\},$$

then shows that the densities must decrease very nearly in the same ratio with the differences of the indices, since I is constant for each substance. A careful examination of the values of the interferential constants given in Table II. shows that in some cases the values diminish very slowly as the temperature increases, suggesting that in these the quantity I is a linear function of the temperature. It will, however, be remarked that the diminution noticed is in the first place extremely small, and secondly that it is not uniformly present. I consider myself, therefore, fully justified in considering I as constant for each substance. In the particular case of carbonic disulphide, I have computed its value for 48° C., which is the boiling-point of the liquid. It will be remarked that, in the case of this substance, the diminution of I with the temperature is quite uniform, but that the total diminution for 48° is only 0.32 % of the value at 0°. It must, furthermore, be remembered that it is scarcely probable that the density of the disulphide can be represented for so great a range of temperature by a linear function. The same remark of course applies to the other liquids examined, though in a less degree. With respect to the determination of I by observation, I may here remark that, although the interference bands between any two spectral lines may be directly counted, so that the spectroscope alone is available, it will still be better, whenever possible, to measure the two indices directly, and then compute I with the assistance of an observed density. It will be seen that τ is for each substance a linear function of the temperature.

For laboratory purposes, the interferential constant will, I hope, like the density, boiling-point, specific volume, &c., serve as a means of recognizing the purity of a given compound. I shall now endeavor to show that it may also find application in quantitative analysis.

The values of I given above are sufficient to prove that the interferential constant of a mixture is the sum of the interferential constants of the component parts. If P be the weight of any mixture, p_1 and p_2 the relative weights of its components, I the constant for the mixture, I_1 and I_2 the constants for the components, we shall have

$$PI = p_1 I_1 + p_2 I_2$$

Table III. contains the values of PI as obtained directly from the observed values of P and I, and also as computed by adding the values of $p_1 I_1$ and $p_2 I_2$ in the cases of all the mixtures cited in Tables I. and II.

TABLE III.

					Percentages.			
Water.	$ZnCl_2$.	PI.	$p_1 I_1 + p_2 I_2$	$\epsilon\%$	Cal'd.	Found.	Cal'd.	Found.
1.0000	3.9970	1201.0	1201.8	+0.06	19.95	19.72	80.05	80.28
1.0000	1.9996	746.1	744.0	—0.27	33.32	34.55	66.68	65.45
1.0000	0.9998	516.4	515.1	—0.27	50.01	51.13	49.99	48.87
Water.	Glycerine *a*.				Water.		Glycerine.	
1.0000	3.7000	1452.3	1451.3	—0.07	21.28	20.56	78.72	79.44
1.0000	1.0000	600.8	601.1	+0.05	50.00	50.52	50.00	49.48
1.0000	0.5000	442.8	443.7	+0.20	66.67	68.64	33.33	31.36
Alcohol.	Glycerine *b*.				Alcohol.		Glycerine.	
1.0000	4.0000	1663.5	1661.1	—0.15	20.00	20.67	30.00	79.33
1.0000	2.0000	1025.7	1025.3	—0.04	33.33	33.52	66.67	66.48
1.0000	0.9980	706.7	706.7	0.00	49.95	50.00	50.05	50.00
1.0000	0.4997	547.5	548.4	+0.16	66.68	65.36	33.32	34.64
Alcohol.	CS_2.				Alcohol.		CS_2.	
1.0000	3 95500	2319.9	2346.4	+1.14	20.18	25.26	79.82	74.74
1.0000	2.12836	1419.3	1442.6	+1.64	31.65	39.03	68.35	66.97
1.0000	1.03111	883.5	899.7	+1.83	49.24	43.21	50.76	56.79

Column 5 gives the differences between the values of PI and $(p_1 I_1 + p_2 I_2)$ in percentages of PI. Columns 6, 7, 8, and 9 give the percentages of the constituents of each mixture, as deduced from the proportions taken by Wüllner and given in Table II., and the percentages as calculated by the formula

$$100\, I = a\, I_1 + (100 - a)\, I_2.$$

In examining Table III., it will be seen that in the cases of mixtures of water and chloride of zinc, of water and glycerine, and of alcohol and glycerine, the differences between the values of PI and $(p_1 I_1 + p_2 I_2)$ in no case exceed 0.27%, and that the signs of the differences are about as often plus as minus. The comparison of the observed and calculated percentages is less satisfactory, but is still sufficient to show that the method is available in analyses of mixtures of liquids in which extreme precision is not required and for which purely chemical methods are wanting.

But with mixtures of alcohol and carbonic disulphide the case is otherwise. The differences between the value of PI and $(p_1 I_1 + p_2 I_2)$ amount as a minimum to 1.14% and as a maximum to 1.83%. I consider it, to say the least, as probable that the mixture of alcohol and the disulphide is accompanied by chemical action resulting in the formation of new compounds. Wüllner found that these mixtures, after standing overnight in well stoppered bottles, gave indices of refraction differing materially from those of the freshly prepared solutions, the differences being too large to be accounted for by a loss of carbonic disulphide. It is difficult to explain this fact in any other way than by supposing that a chemical change begins as soon as the liquids are mixed, though no such change has been observed by chemists.

In any event, my results, I think, render it probable that the method of analysis based upon them will find useful applications. A much larger and more varied series of observations of the indices and densities of different liquids and mixtures of these in various proportions is extremely desirable. For saline solutions, we possess measurements by Sauber, Hoffmann, and others, but unfortunately the densities and indices of refraction have not, except in a very limited number of cases, been determined for the same temperatures. In the particular case of solutions of sugar, Obermayer * has given the following values for the indices of refraction and densities, at 22.26 C.: —

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* Wien. Acad. Ber. 61 (2 Abth.) p. 797.

Line.	10% sol.	20% sol.	30% sol.
C	1.34568	1.36085	1.37800
G	1.35541	1.37167	1.38923
Densities	1.03812	1.08034	1.12639
I	287.4	288.2	289.7
I'	295.4	296.2	300.0

In this table, I gives the interferential constants for the three solutions, I' the constant for the liquid sugar in each, the mean value being 297.2. As the interferential constant for water is 286.2, it is easy to see that nothing is to be hoped for from the employment of the interferential constant as a means of determining the quantity of sugar in a solution, since it is clear that the degree of accuracy to be attained by the method above given, will, in general terms, be in proportion to the difference between the interferential constants of the constituents of the given mixture. In its application to quantitative determinations, the new optical method is analogous to the well-known process of indirect analysis, the success of which depends upon the difference between the atomic weights of the bodies sought. Landolt has shown that the function $\frac{n-1}{d}$ is so nearly constant for a given ray and given substance, that for chemical purposes no very sensible error is made in considering it as absolutely constant. He has further shown that in the case of a mixture of two substances we have very nearly

$$\frac{N-1}{D}P = \frac{n_1-1}{d_1}p_1 + \frac{n_2-1}{d_2}p_2.$$

This expression may be employed for the analysis of mixtures, and in many cases leads to valuable results, as Landolt has sufficiently shown. I am disposed to think that the method which I have proposed above will enable us to obtain a still greater degree of accuracy in cases in which the values of the interferential constants have been determined with the requisite precision.

The valuable data furnished by Wüllner are not the only ones which I have discussed. * Landolt and Haagen have also given a series of measurements of the densities and indices of refraction of a number of liquids. Their results are contained in Table IV.; I have arranged them for convenience in six groups, the sixth group containing the data furnished by Haagen.†

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* Pogg. Annalen, T. 122, p. 545.

† Pogg. Annalen, T. 131, p. 117.

TABLE IV.

Name.	Formula.	Density at 20° C.	Nα.	Nγ.	τ.	I.	MI.
Water	$H_2\ O$	0.9984	1.33111	1.34038	285.7	286.2	51.5
Formic Acid	$C\ H_2\ O_2$	1.2211	1.36927	1.38041	320.4	262.3	120.6
Acetic „	$C_2\ H_4\ O_2$	1.0514	1.36985	1.38017	319.0	303.4	182.0
Propionic „	$C_3\ H_6\ O_2$	0.9963	1.38460	1.39513	331.3	332.5	246 0
Butyric „	$C_4\ H_8\ O_2$	0.9610	1.39554	1.40649	341.9	354.7	312.1
Valeric „	$C_5\ H_{10}\ O_2$	0.9313	1.40220	1.41349	347.0	372.6	380.0
Capronic „	$C_6\ H_{12}\ O_2$	0.9252	1.41164	1.42323	355.2	383.9	445.3
Œnanthic „	$C_7\ H_{14}\ O_2$	0.9175	1.41923	1.43106	361.9	394.4	512.7
Methyl Alcohol	$C\ H_4\ O$	0 7964	1.32789	1.33621	280.9	352.7	112.9
Ethyl „	$C_2\ H_6\ O$	0.8011	1.36054	1.36997	309.5	386.3	177.7
Propyl „	$C_3\ H_8\ O$	0.8042	1.37938	1.38932	325.7	404.9	242.9
Butyl „	$C_4\ H_{10}\ O$	0.8074	1.39395	1.40447	338.7	419.4	310.3
Amyl „	$C_5\ H_{12}\ O$	0.8135	1.40573	1.41689	349.6	429.7	378.1
Methylic Acetate	$C_3\ H_6\ O_2$	0.9053	1.35915	1.36893	309.2	341.5	252.0
Ethylic Formate	$C_3\ H_6\ O_2$	0.9078	1.35800	1.36782	308.4	339.7	251.4
Ethylic Acetate	$C_4\ H_8\ O_2$	0.9021	1.37068	1.38067	318.9	353.5	311.1
Methylic Butyrate	$C_5\ H_{10}\ O_2$	0.8976	1.38693	1 39742	333.2	371.2	378.6
Methylic Valerate	$C_6\ H_{12}\ O_2$	0.8809	1.39272	1.40370	338.8	384.6	446.2
Ethylic Butyrate	$C_6\ H_{12}\ O_2$	0.8906	1.39404	1.40460	338.9	384.8	446.4
Amylic Formate	$C_6\ H_{12}\ O_2$	0.8816	1 39592	1.40689	341.3	387.1	449.0
Ethylic Valerate	$C_7\ H_{14}\ O_2$	0.8674	1.39500	1.40583	322.7	372.0	483.5
Amylic Acetate	$C_7\ H_{14}\ O_2$	0.8574	1.40168	1.41271	346.0	403.5	524.4
Amylic Valerate	$C_{10}\ H_{20}\ O_2$	0.8581	1.40978	1.42124	353.5	411.9	708.4
Aldehyd	$C_2\ H_4\ O$	0.7810	1.32975	1.33937	285.3	365.3	160.7
Valeral	$C_5\ H_{10}\ O$	0.7995	1.38614	1.39729	333.9	417.4	359.0
Acetone	$C_3\ H_6\ O$	0.7931	1.35715	1.36780	309.6	390.3	226.4

TABLE IV. (*continued*).

Name.	Formula.	Density at 20° C.	Nα.	Nγ.	τ.	I.	MI.
Ethylic Ether	$C_4 H_{10} O$	0.7166	1.35112	1.36071	301.7	421.0	311.5
Acetic Anhydrid	$C_4 H_6 O_3$	1.0836	1.38832	1.39927	335.2	309.3	316.4
Ethylene Alcohol	$C_2 H_6 O_2$	1.1092	1.42530	1.43662	365.5	329.5	204.3
Ethylene Acetate	$C_6 H_{10} O_4$	1.1583	1.41932	1.43120	362.0	312.5	456.2
Glycerine	$C_3 H_8 O_3$	1.2615	1.47063	1.48281	403.7	320.0	294.4
Lactic Acid	$C_3 H_6 O_3$	1.2427	1.43915	1.45135	378.6	304.6	274.1
Phenol	$C_6 H_6 O$	1.0722	1.54447	1.57555	506.5	472.4	440.0
Bitter-almond Oil	$C_7 H_6 O$	1.0474	1.53914	1.57749	519.1	495.5	555.2
Salicylous Acid	$C_7 H_6 O_2$	1.1693	1.56467	1.62008	579.1	495.2	604.1
Methyl-salicylous Acid . .	$C_8 H_8 O_3$	1.1824	1.53019	1.56718	508.8	430.3	654.0
Methyl-benzoate	$C_8 H_8 O_2$	1.0882	1.51158	1.53989	473.8	435.4	592.1
Ethyl-benzoate	$C_9 H_{10} O_2$	1.0491	1.50104	1.52749	461.1	439.5	659.2
Carbonic Tetrachloride . .	$C Cl_4$	1.5947	1.457890	1.472900	400.2	250.9	386.4
Chloroform	$C H Cl_3$	1.4930	1.444030	1.458210	387.1	259.2	309.7
Chloride of Ethylene . . .	$C_2 H_4 Cl_2$	1.2562	1.442010	1.455110	383.0	225.2	222.9
Ethylic Bromide	$C_2 H_5 Br$	1.4600	1.421320	1.436290	368.5	252.4	275.1
Amylic Bromide	$C_5 H_{11} Br$	1.2045	1.438560	1.452940	384.8	319.4	482.3
Bromide of Ethylene . . .	$C_2 H_4 Br_2$	2.1827	1.533890	1.556580	478.7	219.3	412.3
Methylic Iodide	$C H_3 I$	2.2636	1.524340	1.553870	486.9	215.0	305.3
Ethylic Iodide	$C_2 H_5 I$	1.9350	1.508120	1.534370	466.3	240.9	375.8
Amylic Iodide	$C_5 H_{11} I$	1.4734	1.487140	1.507080	434.9	295.1	584.3
Phosphorous Chloride . .	$P Cl_3$	1.5774	1.508310	1.524490	443.1	280.9	386.2
Arsenic Chloride	$As Cl_3$	2.1668	1.592000	1.624800	548.4	253.1	459.4
Stannic Chloride	$Sn Cl_4$	2.2328	1.507000	1.531800	462.0	206.9	537.9
Silicic Chloride	$Si Cl_4$	1.4878	1.411900	1.424400	357.6	240.3	408.5
Sodic Chloride	$Na Cl$	2.1543	1.540460	1.560560	477.8	221.8	129.8
Potassic Chloride	$K Cl$	1.9950	1.487270	1.505720	431.6	216.3	161.1

In this Table, the seventh column gives the values of the interferential constant *I*. The eighth is obtained by multiplying the numbers in column six by the molecular weights of the corresponding substances, divided by 100, so as to avoid many figures. The product *M I* gives, therefore, the number of interference bands between *C* and *G* for a thickness of each liquid proportioned to its molecular weight.

I have employed the measurements of Landolt and Haagen in discussing the question whether the interferential constant of a definite chemical compound is the sum of the interferential constants of its constituent atoms. Table V. exhibits the methods and results of this discussion.

TABLE V.

Acids.	*MI*	Δ_1	*C*	Δ_2	$\Delta\%$
$C\,H_2\,O_2$ . . .	120.6		119.7	−0.9	−0.74
		61.4			
$C_2\,H_4\,O_2$ . . .	182.0		184.8	+2.8	+1.53
		64.0			
$C_3\,H_6\,O_2$ . . .	246.0		249.9	+3.9	+1.22
		66.1			
$C_4\,H_8\,O_2$ . . .	312.1		315.1	+3.0	+0.96
		67.9			
$C_5\,H_{10}\,O_2$ . . .	330.0		380.2	+0.2	+0.05
		65.3			
$C_6\,H_{12}\,O_2$ . . .	445.3		445.4	+0.1	+0.02
		67.4			
$C_7\,H_{14}\,O_2$ . . .	512.7		510.5	−2.2	−0.42
	Mean	65.3		Mean	0.70
Alcohols.					
$H_2\,O$ . . .	51.4		50.9	−0.5	−0.97
		61.5			
$C\,H_4\,O$ . . .	112.9		116.2	+3.3	+2.92
		64.8			
$C_2\,H_6\,O$ . . .	177.7		181.2	+3.5	+1.97
		65.2			
$C_3\,H_8\,O$ . . .	242.9		246.3	+3.4	+1.40
		67.4			
$C_4\,H_{10}\,O$ . . .	310.3		311.5	+1.2	+0.38
		67.8			
$C_5\,H_{12}\,O$ . . .	378.1		376.6	−1.5	−0.39
	Mean	65.3		Mean	1.34
Ethers.					
$C_3\,H_6\,O_2$ . . .	251.7		250.0	−1.7	−0.67
		59.4			
$C_4\,H_8\,O_2$ . . .	311.1		313.1	+2.0	+0 64
		67.5			
$C_5\,H_{10}\,O_2$ . . .	378.6		380.2	+1.6	+0.42
		68.6			
$C_6\,H_{12}\,O_2$ . . .	447.2		445.4	−1.8	−0.40
		4 × 65.3			
$C_{10}\,H_{20}\,O_2$ . . .	708.4		705.9	−2.5	−0.35
	Mean	65.2		Mean	0 50

In this table, column second gives the interferential equivalent of the liquid, the formula of which is given in column first. Column Δ_1 gives the differences of the interferential equivalents for the constant chemical difference CH_2; the liquids of each group being homologous. It will be at once seen that Δ_1 is not constant in any one group, but increases with the molecular weight of the liquid. From this it follows that the interferential equivalents of either carbon or hydrogen, or of both, are variable. The last case is most probable. The mean of the differences Δ_1 is the same for all these groups. From the above it is easy to see that in the strict sense neither carbon nor hydrogen can be said to possess a constant interferential equivalent. As it seemed, however, practicable in this case, as in the case of the refractive equivalents, to deduce, at least, an available rule for computing approximately the interferential equivalent of a compound from the equivalents of its constituent atoms, I determined the equivalents of carbon, hydrogen, and oxygen by means of the data given in Table V. and obtained the following values: —

Carbon	41.46
Hydrogen	11.84
Oxygen	27.28

With these values I computed the numbers of column *C* in Table V. and of the fourth column in Table VI.

TABLE VI.

Name.	Formula.	Found.	Calc'd.	Δ_2	$\Delta\%$
Aldehyd . . .	$C_2 H_4 O$	160.7	157.6	—3.1	—1.92
Valeral	$C_5 H_{10} O$	359.0	353.0	—6.0	—1.69
Acetone . . .	$C_3 H_6 O$	226.4	222.7	—3.7	—1.63
Ethyl-ether . .	$C_4 H_{10} O$	311.5	311.5	0.0	0.00
Acetic Anhyd. .	$C_4 H_6 O_3$	316.4	318.7	+2.3	+0.72
Ethylen Alc. . .	$C_2 H_6 O_2$	204.3	208.5	+4.2	+2.05
Biacet. ethylene .	$C_6 H_{10} O_2$	456.2	476.2	+20.0	+4.39
Glycerine . . .	$C_3 H_8 O_3$	294.4	300.9	+5.5	+1.86
Lactic Acid . .	$C_3 H_6 O_3$	274.1	277.3	+3.2	+1.17
				Mean	1.58

In these tables, column Δ_2 gives the differences between the observed and computed values in the case of each liquid, and column $\Delta\%$ the same differences in percentages of the observed values. The means of these last are also given without reference to sign. With the aid of the equivalents of carbon and hydrogen, I determined those of chlorine, bromine, and iodine, given in Table VIII. Finally, the equivalents of carbon and chlorine gave those of the other elements in the same table. Columns fourth, fifth, and sixth, in Table VII., have the same signification as the corresponding columns of Tables V. and VI.

TABLE VII.

Name.	Formula.	Found.	Calc'd.	$\triangle_2$	$\triangle\%$
Carbonic tetrachloride	$C\ Cl_4$	386.4	384.8	—1.6	—0.41
Chloroform	$C\ H\ Cl_3$	309.7	310.8	+1.1	+0.35
Ethylic bromide . .	$C_2\ H_5\ Br$	275.1	281.7	+6.6	+2.39
Amylic bromide . .	$C_5\ H_{11}\ Br$	482.3	477.1	—5.2	—1.08
Ethylene bromide . .	$C_2\ H_4\ Br_2$	412.3	409.5	—2.8	—0.67
Methylic iodide . . .	$C\ H_3\ I$	305.3	313.3	+8.0	+2.62
Ethylic iodide . . .	$C_2\ H_5\ I$	375.8	378.4	+2.6	+0.69
Amylic iodide . . .	$C_5\ H_{11}\ I$	584.3	573.8	—10.5	—1.79
Carbon disulphide .	$C\ S_2$	375.7			
Phosphorous chloride	$P\ Cl_3$	386.2		Mean	1.25
Arsenous chloride . .	$As\ Cl_3$	459.4			
Stannic chloride . .	$Sn\ Cl_4$	537.9			
Silicic chloride . . .	$Si\ Cl_4$	408.5			
Sodic chloride . . .	$Na\ Cl$	129.8			
Potassic chloride . .	$K\ Cl$	161.1			

TABLE VIII.

Carbon	41.46	Phosphorus . . .	128.70
Hydrogen . . .	11.84	Arsenic	201.90
Oxygen	27.28	Tin	194.50
Chlorine	85.85	Silicon	65.10
Bromine	139.60	Potassium . . .	75.29
Iodine	236.30	Sodium	44.00
Sulphur	167.12		

The results tabulated in V., VI., and VII., are sufficient to show that the interferential equivalents of compounds may, in many cases, be computed with a tolerably close approximation from those of the constituent atoms. The approximation is, however, much less close than in the cases of mixtures. On the other hand, the rule fails entirely with certain compounds. Thus, the six liquids of the aromatic series forming group fifth of Table IV., present very marked exceptions. In these cases, no values of the interferential equivalents of carbon, hydrogen, and oxygen, can be found which will enable us to compute the molecular equivalents. Mr. Gladstone * has met with similar exceptions in the refractive equivalents of the benzol series, and suggests,

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* Journal of the Chemical Society [2] Vol. 8, p. 101.

in substance, that these are probably due to the fact that, optically, each molecule may be regarded as composed of groups of atoms, each group possessing a specific optical character. So far as the interferential equivalents are concerned, further data are necessary to enable us to test this explanation.

Landolt has given the densities and indices of refraction of a number of mixtures. I have not discussed these results from my own point of view, because since the publication of his work the progress of organic chemistry has shown that many of the substances with which Landolt dealt could not have been absolutely pure, though prepared with great care for the special purpose of his investigation.* I think I have shown that the so-called interferential constants possess a real value as numerical characteristics easily determined by measurements of two indices of refraction and a single observation of density at the same temperature. But the value of the new constants in quantitative analyses can only be fairly estimated when we possess determinations of indices and densities for a series of mixtures for which the proportions, densities, and indices of the constituents are accurately known. The time has also arrived when a much greater degree of accuracy in the determination of indices of refraction is necessary. Even five decimal places do not answer the present requirements of science. Six are attainable with spectrometers reading to two seconds of arc.

It is easy to see that the numerical value of an interferential constant depends in part upon the angular distance of the spectral lines between which the bands are counted. The lines *C* and *G* are particularly well adapted for standard limits, as they are hydrogen lines always obtainable by a small Ruhmkorff coil and hydrogen tube. The interferential constant may be taken as a measure of the dispersive power of a body; and it is readily shown that with this measure, also, the total dispersive power from *A* to *H* is the sum of the partial dispersions from *A* to *B*, *B* to *C* . . . *G* to *H*. The theory and construction of achromatic lenses might also be based upon this measure of dispersive power, but it would probably possess no practical advantages over the ordinary method.

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* I refer to the improvements in separating liquids of different boiling-points introduced by Linnemann, — improvements which have shown that up to the period of his work we had no really accurate knowledge of the boiling-points of a number of liquids long known to science, but never before obtained in a state of perfect purity.

II. — ON A METHOD OF MEASURING REFRACTIVE INDICES WITHOUT THE USE OF DIVIDED INSTRUMENTS.

The importance of an accurate determination of all the physical constants which characterize any substance having a definite chemical constitution becomes daily more and more evident. The researches of Gladstone, Landolt, and others have shown that indices of refraction possess a peculiar value and interest. As the instruments necessary for their determination are expensive, and often beyond the reach of working chemists, a simple and sufficiently accurate method of measuring them by means of the spectroscope alone will doubtless be welcomed.

The method which I propose is one of comparison, and applies with convenience only to the case of liquids. A hollow prism is to be filled with the liquid to be examined, placed upon the stage of the spectroscope, and turned until a given ray — the line *D*, for instance — is seen by the observing telescope to be in the position of minimum deviation. The eye-piece of the telescope should have two parallel spider-lines placed very near each other in the plane of the diaphragm. When the dispersion is sufficiently great to separate the line *D* into its two components, either component may be made to bisect the interval between the two spider-lines, or the two components may be made to occupy such positions that their middle line shall bisect the interval. The observing telescope is then to be firmly clamped. The prism is now to be removed, the liquid poured out, and the prism cleaned and dried carefully. It is then to be filled with any liquid the indices of refraction of which are known, and which the observer judges to have a mean index not greatly differing from that of the liquid to be measured. The prism is to placed upon the stage of the spectroscope, and turned until the observer ascertains that the two spectra would be in the field of view if both could be seen at the same time; or, what is the same thing, that they would be more or less completely superposed. Should this not be the case, another comparison-liquid must be chosen; and so on until one is found which fulfils the requisite conditions. Supposing that this is successfully accomplished, the prism is to be turned until, for the position of minimum deviation, a known line in the spectrum exactly bisects the interval between the two spider-lines. The index of refraction of the given liquid for the line *D* is then the same as that of the known line in the spectrum of the liquid used for comparison; for we have for each case

$$n = \frac{\sin \frac{1}{2}(P + D)}{\sin \frac{P}{2}} \quad n' = \frac{\sin \frac{1}{2}(P + D')}{\sin \frac{P}{2}}$$

and, since P is constant, and $D' = D$, it follows that $n' = n$.

By this method, the index of refraction of a given liquid may be determined for a single line; as, for instance, for D. This is sufficient for the optical analysis in the form in which it has been developed by Landolt. Two objections to this method present themselves at once. The first is the necessity of finding by tentative processes a comparison-liquid which shall have about the same mean index of refraction as the liquid an index of which is to be determined. I admit the force of the objection, but it must not be estimated too highly. Whole classes of liquids agree pretty nearly in their optical characters; as, for instance, the oils of the $C_{10}H_{16}$ series, the ethers of the fatty acids, hydrocarbons and saline solutions. The second objection is that, with liquids of low dispersive powers, it is not easy to distinguish the spectral lines with absolute certainty. This difficulty is easily avoided by using a second prism, with a high dispersive power, placed next to the collimator so as to form a long spectrum, which shall fall upon the trial-prism. The final dispersion is then the sum of the dispersions of the two prisms, and no difficulty will be found in distinguishing the spectral lines. It is, of course, necessary that the subsidiary prism shall have the same position in both cases. Two or more subsidiary prisms either of flint-glass or of carbonic disulphide may be used with great advantage, but one will usually be found sufficient. The indices of refraction of the comparison-liquids being known for at least three lines, the values of the constants a, b, and c in Cauchy's formula

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

may be determined. It then only remains to compute the index of refraction of the line which has been found to have the same index as the line D, for instance, of the liquid examined. This is easily done when the line in question has been identified by means of Kirchhoff's chart so that its wave-length is known. It will, of course, often happen that no line in the comparison-liquid exactly corresponds with the line D selected for the liquid examined. In this case the index of the nearest line may be employed instead, when great accuracy is not required and when subsidiary prisms are used, or we may use a filar micrometer, and interpolate so as to obtain the index of a coincident line by measuring the distance of the relative line *D* from one or more visible lines in the comparison-spectrum. The eye-piece micrometer suggested by Professor Rood * would also give all necessary precision, and would have the advantage of being very much cheaper than a filar micrometer.

The method above given enables us to determine the index of refraction of a single line only, unless the prism is emptied, cleaned, dried, and the operation then repeated with a second selected line. To obviate this difficulty, I have employed the following modification of the prism with entire success. The prism is divided into two by a septum perpendicular to its refracting edge. Each prism thus formed has an opening in its base by which liquid may be introduced or removed, and which can be closed with a cork. When the two glass plates are carefully cemented to the brass frame, the two prisms will have the same refracting angle. One of them is then to be filled with the comparison-liquid, the other with the liquid the indices of which are to be determined. The double prism being now placed upon the stage of the spectroscope, one face of the prism containing the comparison-liquid is to be covered with a slip of metal. The spectrum of the liquid to be examined will then be seen by means of the observing telescope. Any line — as, for instance, *C* — may then be selected, brought into the position of minimum deviation, and the telescope adjusted until this line bisects the space between the parallel wires in the plane of the diaphragm of the eye-piece. The telescope is then to be clamped as before without disturbing the adjustment. If now one face of the prism containing the liquid examined be covered with the slip of metal removed from the face of the other prism, the spectrum of the comparison-liquid will be seen, and it will be easy to determine what line in this spectrum most nearly corresponds in position to the line *C* of the other spectrum. By alternately covering the faces of the two prisms with the metal slip, coincidences or near coincidences may be observed for *D*, *E*, *F*, &c.; and in this manner the data obtained for the constants in Cauchy's dispersion-formula for the liquid examined, in a short time and with great facility. It must be borne in mind that the two spectra in this process cannot be seen simultaneously, their images being combined by the observing telescope into one.†

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* Am. Journal, 3d series, vol. vi. p. 44.

† Mr. S. P. Sharples has suggested to me that if a cylindrical lens were employed as the object-glass of the observing telescope, the two spectra could be seen in the field at the same time.

In applying the above methods, I have used prisms with brass frames, and have cemented the glass-plates either with common or with marine glue, the latter being employed for aqueous solutions. Good workmanship would doubtless make it possible to fit the plates to the sides of the prisms so that they could be held in their places by springs, the prisms being perfectly tight; but I have not found this to be the case with prisms from German workshops which I have examined.

The process which I have given above furnishes, of course, a new application of the spectroscope to quantitative chemical analysis, — all the results obtained by Landolt with the spectrometer being obtained with the spectroscope alone; but it is hardly necessary to say that a good spectrometer is an instrument greatly to be preferred, since it may be used also as a spectroscope, and since direct methods are always better than those of comparison.